CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Reversible Dimerization of Mononuclear Models of [Fe]-Hydrogenase

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A. Chemicals and Reagents

All manipulations were carried out under an inert N_2(g) atmosphere using a Schlenk line. Solvents were distilled from appropriate drying agents under N_2 before use. The reagents including all the thiols were purchased from commercial sources. Liquid compounds were degassed by standard freeze-pump-thaw procedures prior to use. Complexes [(6-MeO-C_5H_3N-2-CH_2CO)Fe$(CO)_2${S-(2,6-$Me_2C_6H_3$)}] (**1**)[S1] [(2-CH_2CO-6-$MeOC_5H_3N$)Fe$(CO)_3$I] (**2**)[S1] and [(6-MeO-C_5H_3N-2-CH_2CO)Fe$(CO)_2(CH_3CN)_2$](BF_4) (**6**)[S2] were prepared as described previously.

B. Physical methods

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si (δ = 0 ppm). The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm), or CD_3CN (1.2 and 118.3 ppm). IR spectra were recorded as KBr disks on a Bruker Alpha FT-IR spectrometer or a Nicolet iS5 FT-IR Spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer or a Carlo Erba EA 1110 CHN instrument. X-ray diffraction studies were carried out in the EPFL Crystallographic Facility. Data collections were performed at low temperature using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption.[S3] Solution, refinement and geometrical calculations for all crystal structures were performed by SHELXTL.[S4]

C. Synthetic methods

Reaction of complex **2** with (4-NO_2-C_6H_4)SNa

A newly synthesized sample of (4-NO_2-C_6H_4)SNa (66.2 mg, 0.374 mmol), which was prepared by NaH (9.0 mg, 0.374 mmol) and (4-NO_2-C_6H_4)SH (58.0 mg, 0.374 mmol) in THF, was mixed with complex **2** (156.0 mg, 0.374 mmol) in CH_2Cl_2 (10 mL). After stirring for 0.5 h at room temperature in the dark, the solvent was evaporated in vacuum during 0.5 h. The residue was extracted with CH_2Cl_2 (2 mL). After removing the solvent of the filtrate, the residue was recrystallized from CH_2Cl_2/hexane at -30 °C in the dark to afford **3a** (90.0 mg, 0.108 mmol, 58%) as orange crystals. The color of its solution (**3a'**) is also orange.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.83 (t, *J = 7.6 Hz*, 1H), 7.79 (d, *J = 6.8* Hz, 2H), 7.29 (br s, 2H), 7.06 (d, *J = 7.6 Hz*, 1H), 6.82 (d, *J = 7.6 Hz*, 1H), 4.52 (d, *J = 20.0 Hz*, 1H), 3.88 (m, 4H) ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$, -30 ^{o}C.): 8.11 (d, *J* = 8.4 *Hz*, 2H), 7.93 (t, *J* = 8.0 *Hz*, 1H), 7.73 (d, *J* = 8.4 *Hz*, 2H), 7.14 (d, *J* = 8.0 *Hz*, 1H), 6.62 (d, *J = 8.0 Hz*, 1H), 4.40 (d, *J = 20.0 Hz*, 1H), 3.65 (d, *J = 20.0 Hz*, 1H), 3.51 (s, 3H) ppm. IR ($\nu_{CO,}$ solid, cm^{-1}): 2024 (s), 2007 (s), 1977 (s), 1962 (s). IR ($\nu_{CO,}$ CH_3CN, cm^{-1}): 2032 (s), 1973 (s). IR ($\nu_{CO,}$ $CHCl_3$, cm^{-1}): 2038 (s), 1977 (s). Anal. Calcd for $C_{32}H_{24}Fe_2N_4O_{12}S_2$: C, 46.2; H, 2.9; N, 6.7. Found: C, 45.9; H, 2.9, N, 6.6.

Analogous reactions of **2** with PhSNa, (2-MeC_6H_4)SNa, (2-EtC_6H_4)SNa, (2-*i*-PrC_6H_4)SNa, (2-OMe-C_6H_4)SNa and (4-MeC_6H_4)SNa, did not yield isolable products.

Reaction of **3a'** with CO

A solution of **3a'** (5.0 mg, 0.0077 mmol) in 0.5 mL CD_3CN or $CHCl_3$ was added to a J Young NMR tube. The solution was frozen and the tube was evacuated under vacuum. 1 atm of CO was added and the tube was sealed. The NMR showed [(6-MeO-C_5H_3N-2-CH_2CO)$Fe(CO)_3$(S-(4-NO_2-C_6H_4))] (**5a**) formed. If the tube was opened and flushed with N_2, **5a** would transform back to **3a'**.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.86 (t, *J = 8.0 Hz*, 1H), 7.79 (d, *J = 8.0 Hz*, 2H), 7.25 (d, *J = 8.0 Hz*, 2H), 7.15 (d, *J = 8.0 Hz*, 1H), 6.85 (d, *J = 8.0 Hz*, 1H), 4.69 (d, *J = 20.0 Hz*, 1H), 4.04 (d, *J = 21.2 Hz*, 1H), 3.88 (s, 3H) ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$, -30 ^{o}C.): 8.00-7.82 (m, 3H), 7.26 (m, 3H), 6.77 (d, *J = 7.2 Hz*, 1H), 4.96 (d, *J = 21.2 Hz*, 1H), 4.17 (d, *J = 21.2 Hz*, 1H), 3.95 (s, 3H) ppm. IR ($\nu_{CO,}$ CH_3CN, cm^{-1}): 2083 (s), 2034 (s), 2008 (s).

Decomposition reaction of **3a'**

A solution of **3a'** (5.0 mg, 0.0077 mmol) in 0.5 mL $CDCl_3$ was added to a J Young NMR tube. The tube was put in the dark at room temperature. The reaction was monitored by ^{1}H NMR at -30 ^{o}C. After 1h, about half of **3a'** was decomposed. After 2 h, almost all was decomposed. One of the species in the mixture was identified as **5a** according to the ^{1}H NMR spectra.

Reaction of complex **2** with (2-F-C_6H_4)SNa

(2-F-C_6H_4)SNa (70.3 mg, 0.469 mmol), which was prepared by NaH (11.3 mg, 0.469 mmol) and (2-F-C_6H_4)SH (60.0 mg, 0.374 mmol) in THF, was mixed with complex **2** (195.5 mg, 0.469 mmol) in CH_2Cl_2 (10 mL). After stirring for 0.5 h at room temperature in the dark, the solvent was evaporated in vacuum for 0.5 h. The residue was extracted with CH_2Cl_2 (2 mL). After removing the solvent of the filtrate,

the residue was recrystallized from CH_2Cl_2/hexane at -30 °C in the dark to afford **3b** (80.0 mg, 0.103 mmol, 44%) as yellow crystals. The color of its solution (**3b'**) is red.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.85 (t, *J = 8.0 Hz*, 1H), 7.12 (d, *J = 6.8* Hz, 1H), 7.04 (m, 2H), 6.87 (t, *J = 8.0 Hz*, 1H), 6.79 (m, 2H), 4.60 (d, *J = 20.0 Hz*, 1H), 3.98 (d, *J = 20.0 Hz*, 1H), 3.80 (s, 3H) ppm. IR ($\nu_{CO,}$ solid, cm^{-1}): 2031 (s), 2011 (s), 1980 (s), 1965 (s). IR ($\nu_{CO,}$ $CHCl_3$, cm^{-1}): 2036 (s), 1975 (s). Anal. Calcd for $C_{32}H_{24}F_2Fe_2N_2O_8S_2$•0.6$CH_2Cl_2$: C, 47.2; H, 3.1; N, 3.4. Found: C, 47.0; H, 2.8, N, 3.4.

Reaction of complex **2** with (2,4-F_2-C_6H_3)SNa

(2,4-F_2-C_6H_3)SNa (73.6 mg, 0.438 mmol), which was prepared by NaH (10.5 mg, 0.469 mmol) and (2,4-F_2-C_6H_3)SH (64.0 mg, 0.438 mmol) in THF, was mixed with complex **2** (182.8 mg, 0.438 mmol) in CH_2Cl_2 (10 mL). After stirring for 0.5 h at room temperature in the dark, the solvent was evaporated in vacuum for 0.5 h. The residue was extracted with CH_2Cl_2 (2 mL). After removing the solvent of the filtrate, the residue was recrystallized from CH_2Cl_2/hexane at -30 °C in the dark to afford **3c** (90.0 mg, 0.111 mmol, 50%) as yellow crystals. The color of its solution (**3c'**) is red.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.84 (t, *J = 8.0 Hz*, 1H), 7.09 (d, *J = 6.8* Hz, 1H), 6.95 (s, 1H), 6.77 (m, 2H), 6.62 (br s, 1H), 4.53 (d, *J = 20.0 Hz*, 1H), 3.90 (d, *J = 20.0 Hz*, 1H), 3.80 (s, 3H) ppm. IR ($\nu_{CO,}$ solid, cm^{-1}): 2028 (s), 2004 (s), 1986 (s), 1961 (s). IR ($\nu_{CO,}$ CH_3CN, cm^{-1}): 2030 (s), 1967 (s). Anal. Calcd for $C_{32}H_{22}F_4Fe_2N_2O_8S_2$: C, 47.2; H, 2.7; N, 3.4. Found: C, 47.2; H, 2.4, N, 3.5.

Reaction of complex **2** with (2-CF_3-C_6H_4)SNa

(2-CF_3-C_6H_4)SNa (83.2 mg, 0.416 mmol), which was prepared by NaH (10.0 mg, 0.416 mmol) and (2,4-F_2-C_6H_3)SH (74.0 mg, 0.416 mmol) in THF, was mixed with complex **2** (173.4 mg, 0.416 mmol) in CH_2Cl_2 (10 mL). After stirring for 0.5h at room temperature in the dark, the solvent was evaporated in vacuum for 0.5 h. The residue was extracted with CH_2Cl_2 (2 mL). After removing the solvent of the filtrate, the residue was recrystallized from CH_2Cl_2/hexane at -30 °C in the dark to afford a mixture of **3d'** and **5d** (85 mg) as red solid. The color of the solution is also red. The ^{1}H NMR at room temperature only shows averaged signals because the equilibrium between **3d'** and **5d** is so fast. From the ^{1}H NMR at -30 ^{o}C, the ratio is about 5:4.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.94 (t, *J = 8.0 Hz*, 1H), 7.53 (br s, 1H), 7.19 (m, 2H), 7.03 (br s, 1H), 6.94 (d, *J = 8.0* Hz, 1H), 4.63 (d, *J = 20.0 Hz*, 1H), 4.00 (d, *J = 20.0 Hz*, 1H), 3.90 (s, 3H) ppm.

Reaction of the mixture of **3d'** and **5d** with CO

A solution of the mixture of **3d'** and **5d** in 0.5 mL CD_3CN was added to a J Young NMR tube. The solution was frozen and the tube was evacuated under vacuum. 1 atm of CO was added and the tube was sealed. The NMR showed the mixture turned into **5d**.

^{1}H NMR (400.13 MHz, CD_3CN, -30 ^{o}C.): 7.98 (t, *J = 8.0 Hz*, 1H), 7.55 (d, *J = 8.0 Hz*, 1H), 7.29-7.15 (m, 3H), 6.98 (d, *J = 8.0 Hz*, 1H), 6.54 (d, *J = 8.0 Hz*, 1H), 4.80 (d, *J = 21.2 Hz*, 1H), 4.22 (d, *J = 21.2 Hz*, 1H), 3.83 (s, 3H) ppm. ^{13}C NMR (100.62 MHz, CD_3CN, -30 ^{o}C): 262.0 (CH_2***C***O), 209.4 (terminal ***C***O), 205.6 (terminal ***C***O), 201.9 (terminal ***C***O), 165.4, 161.5, 142.3, 139.5, 131.8, 126.7, 126.3, 116.1, 105.5, 65.2, 56.5 ppm. IR ($\nu_{CO,}$ CH_3CN, cm^{-1}): 2085 (s), 2035 (s), 2008 (s).

Reaction of complex **6** with (2-CF_3-C_6H_4)SH and NEt_3

(2-CF_3-C_6H_4)SH (49.5 mg, 0.278 mmol) and complex **6** (120.0 mg, 0.278 mmol) were mixed in CH_3CN (2 mL). NEt_3 (28.1 mg, 0.278 mmol) was added into the mixture at -30 ^{o}C. The color turned form yellow to red immediately. The solvent was evaporated and a mixture of CH_2Cl_2 (0.5 mL) and ether (10 mL) was added to extract the residue. The filtrate was evaporated in vacuum and recrystallized from CH_2Cl_2/hexane at -30 °C in the dark to afford **3d'** (60.0 mg, 0.137 mmol, 49%) as red solid. The color of the solution is also red.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.95 (t, *J = 8.0 Hz*, 1H), 7.53 (t, *J = 5.2 Hz*, 1H), 7.20 (m, 3H), 7.07 (br s, 1H), 6.95 (d, *J = 8.0* Hz, 1H), 4.63 (d, *J = 20.0 Hz*, 1H), 3.99 (d, *J = 20.0 Hz*, 1H), 3.90 (s, 3H) ppm. IR ($\nu_{CO,}$ solid, cm^{-1}): 2025 (s), 1962 (s). IR ($\nu_{CO,}$ CH_3CN, cm^{-1}): 2030 (s), 1967 (s). Anal. Calcd for $C_{17}H_{12}F_3FeNO_4S$: C, 46.5; H, 2.8; N, 3.2. Found: C, 46.2; H, 2.7, N, 3.4.

Reaction of complex **6** with *t*-BuSH and NEt_3

t-BuSH (30.2 mg, 0.336 mmol) and complex **6** (140.0 mg, 0.336 mmol) were mixed in a mixture of CH_3CN (0.2 mL) and CH_2Cl_2 (1 mL). NEt_3 (33.9 mg, 0.336 mmol) was added into the mixture at -60 ^{o}C. The color turned form yellow to red immediately. Cold hexane (20 mL, -60 ^{o}C) was added into this solution immediately, and the precipitate was collected and dried in vacuum to afford a mixture of **3e** and $[NEt_3H]BF_4$ as a yellow solid. The color of the solution is red.

^{1}H NMR (400.13 MHz, CD_3CN, r.t.): 7.92 (t, *J = 8.8 Hz*, 1H), 7.16 (d, *J = 8.8 Hz*, 1H), 6.95 (d, *J = 8.8* Hz, 1H), 4.47 (d, *J = 20.8 Hz*, 1H), 4.00 (m, 4H), 1.33 (s, 9H) ppm. IR ($\nu_{CO,}$ solid, cm^{-1}): 2025 (s), 1994 (s), 1955 (s), 1934 (s). IR ($\nu_{CO,}$ CH_3CN, cm^{-1}): 2015 (s), 1951 (s).

Other methods to get **3e**, such as the transthiolation reaction of **1** with *t*-BuSH, and the metathesis reaction of [(2-CH_2CO-6-$MeOC_5H_3N$)$Fe(CO)_3I$] (**2**) with *t*-BuSNa, were unsuccessful.

D. Crystallographic Details for 3a

A total of 53375 reflections (-11 ≤ *h* ≤ 11, -24 ≤ *k* ≤ 25, -18 ≤ *l* ≤ 18) were collected at *T* = 100(2) K in the range of 3.00 to 24.22° of which 5903 were unique (R_{int} = 0.2000); $Mo_{K\square}$ radiation (λ= 0.71073 Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.943 and –0.668 eA^{-3}, respectively. The absorption coefficient was 1.106 mm^{-1}. The least squares refinement converged normally with residuals of *R*(*F*) = 0.0926, *wR*(F^2) = 0.2016 and a GOF = 1.039 ($I>2\sigma(I)$). $C_{32}H_{24}Cl_2Fe_2N_2O_{12}S_2$, Mw = 875.25, space group $P2_1/c$, Monoclinic, *a* = 10.312(2), *b* = 22.019(3), *c* = 16.272(3) Å, β = 90.918(15) °, *V* = 3694.3(11) $Å^3$, *Z* = 4, ρ_{calcd} = 1.574 Mg/m^3. CCDC-919373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

E. Crystallographic Details for 3b

A total of 32008 reflections (-13 ≤ *h* ≤ 13, -17 ≤ *k* ≤ 17, -17 ≤ *l* ≤ 17) were collected at *T* = 100(2) K in the range of 3.05 to 27.50° of which 8043 were unique (R_{int} = 0.0512); $Mo_{K\square}$ radiation (λ= 0.71073 Å). The structure was solved by the direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.448 and –0.450 eA^{-3}, respectively. The absorption coefficient was 1.155 mm^{-1}. The least squares refinement converged normally with residuals of *R*(*F*) = 0.0387, *wR*(F^2) = 0.0706 and a GOF = 1.103 ($I>2\sigma(I)$). $C_{33}H_{26}FeCl_2F_2Fe_2N_2O_8S_2$, Mw = 863.28, space group *P*-1, Triclinic, *a* = 10.0741(10), *b* = 13.4627(18), *c* = 13.7880(18) Å, α = 80.019(11) °, β = 75.419(9) °, γ = 79.916(9), *V* = 1765.5(4) $Å^3$, *Z* = 2, ρ_{calcd} = 1.624 Mg/m^3. CCDC-919372 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

(S1) Chen, D. F.; Scopelliti, R.; Hu, X. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 5671-5673.

(S2) Chen, D. F.; Scopelliti, R.; Hu, X. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 1919-1921.

(S3) Blessing, R. H. *Acta Crystallogr*. *A* **1995**, *51*, 33-38.

(S4) Sheldrick, G. M. *SHELXTL* release 6.1.4 ed.; Bruker AXS Inc.: Madison, Wisconsin, 53719, USA, 2003.

Crystal Structure

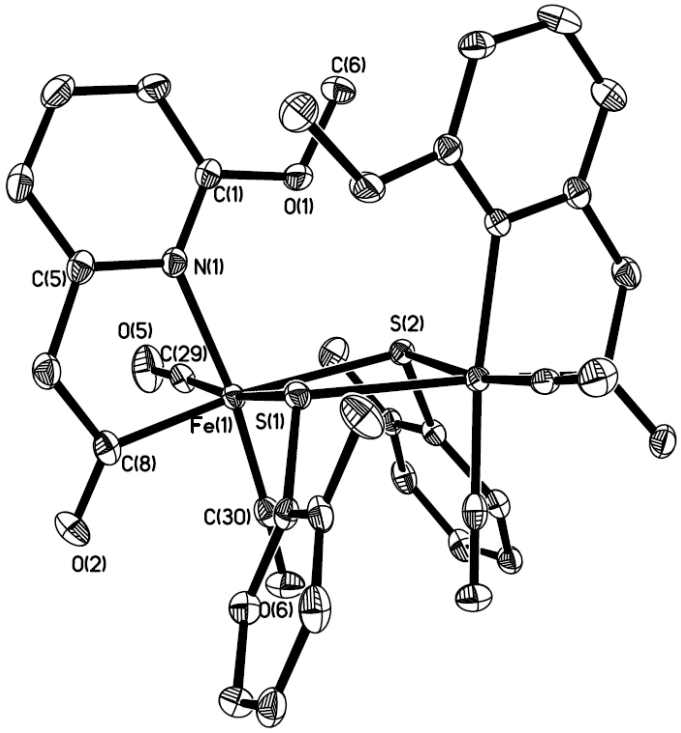

Figure S1. Solid-state molecular structure of complex **3b**. The thermal ellipsoids are displayed at 50% probability. Selected bond distances (Å) and angles (^{o}): Fe1-N1, 2.0765(19); Fe1-C8, 1.945(2); Fe1-C29, 1.799(2); Fe1-C30, 1.762(2); Fe1-S1, 2.3435(7); Fe1-S2, 2.5160(7); C29-Fe1-C30, 89.76(11); C8-Fe1-N1, 83.86(9).

IR spectra

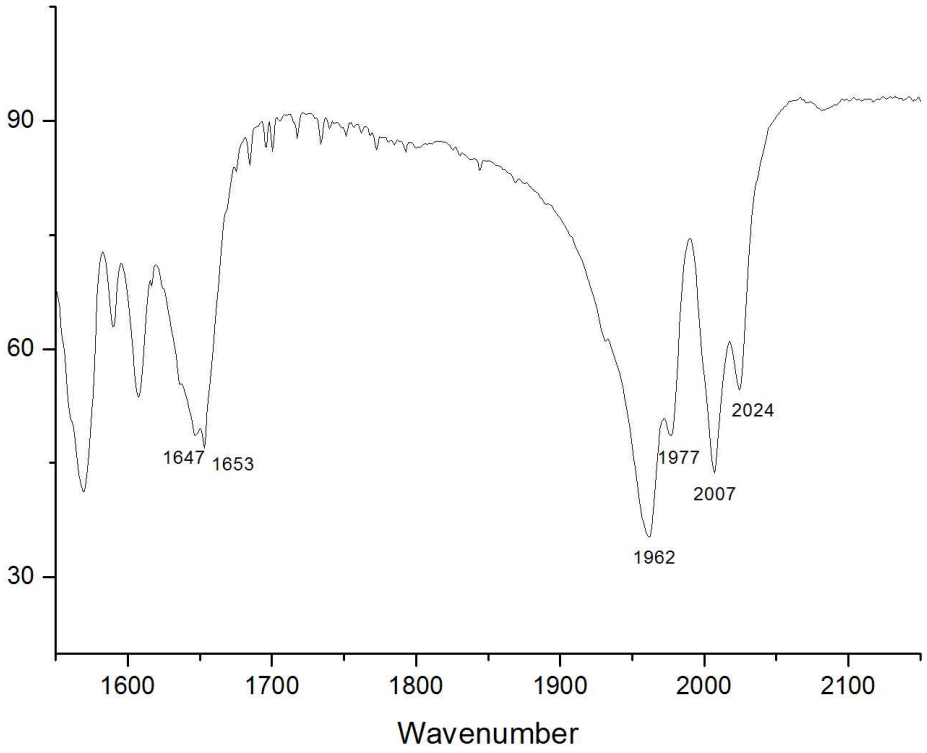

Figure S2. IR spectrum of **3a** in the solid state.

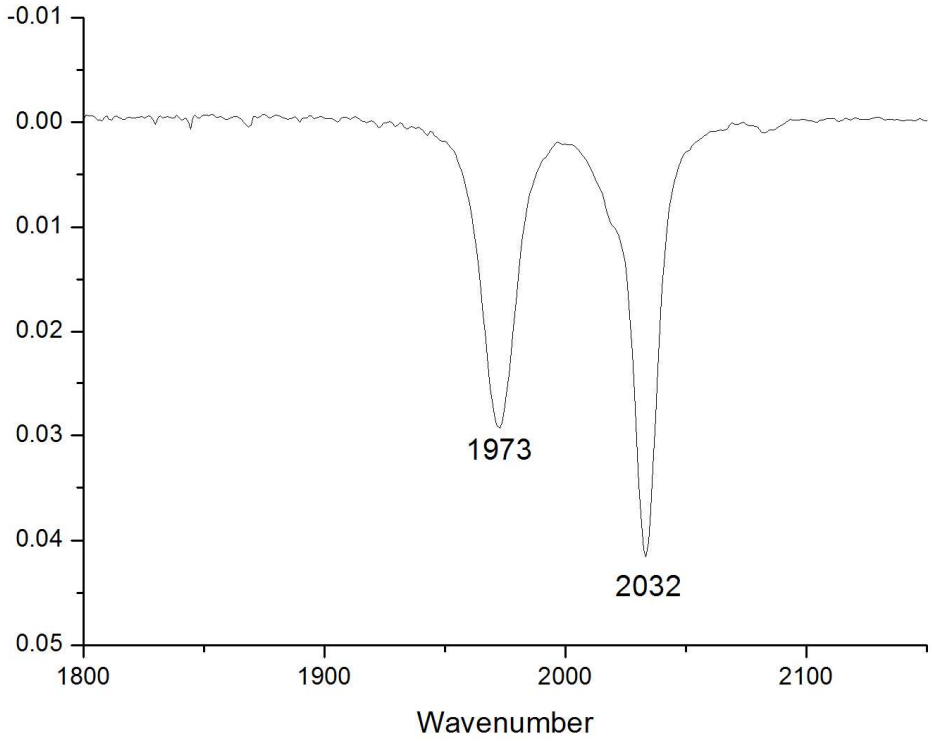

Figure S3. IR spectrum of **3a'** in CH_3CN.

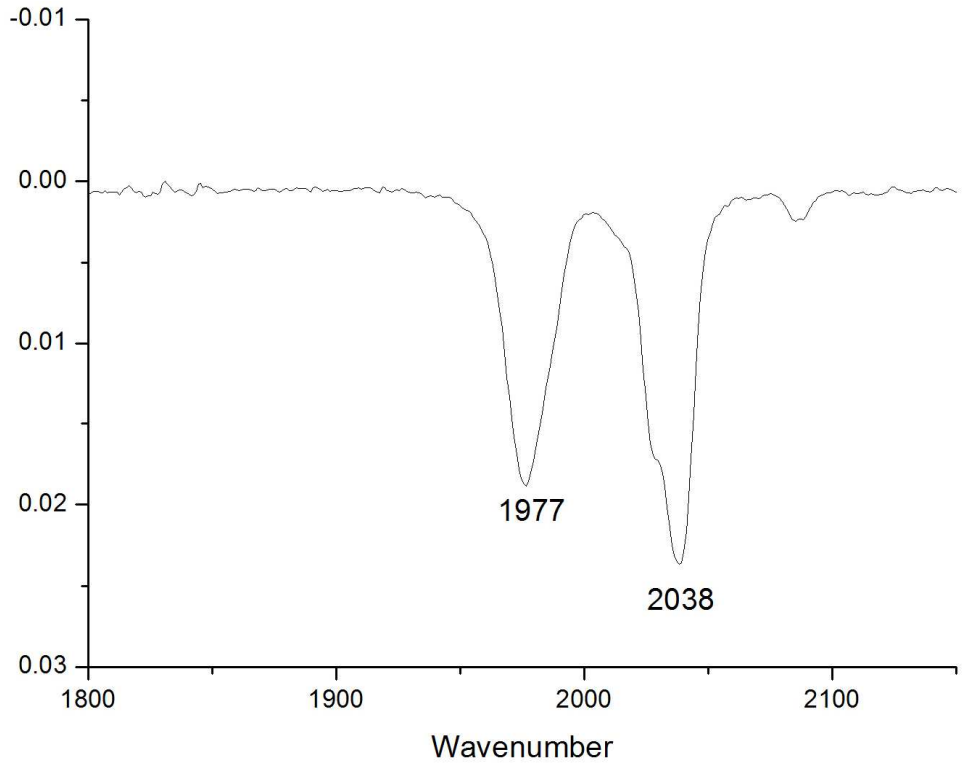

Figure S4. IR spectrum of **3a'** in $CHCl_3$.

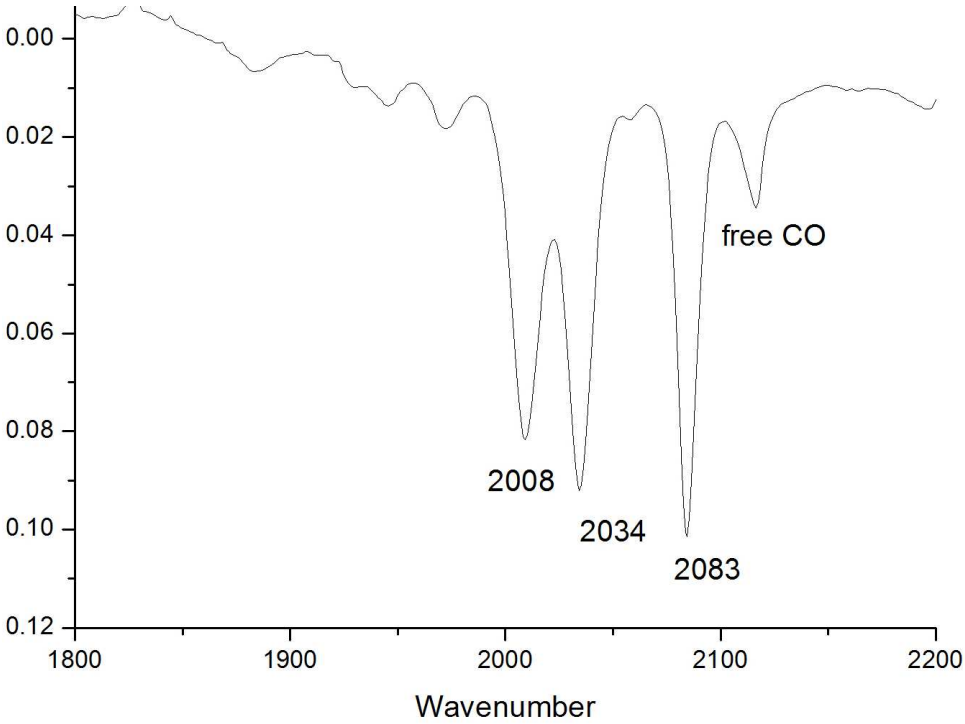

Figure S5. IR spectrum of **5a** in CH_3CN.

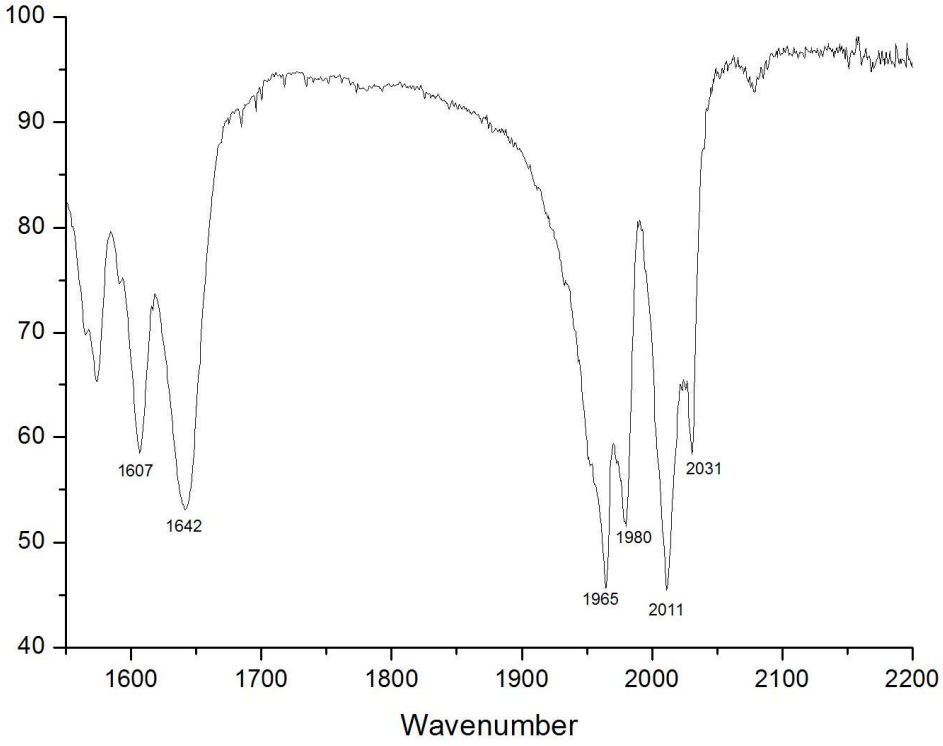

Figure S6. IR spectrum of **3b** in the solid state.

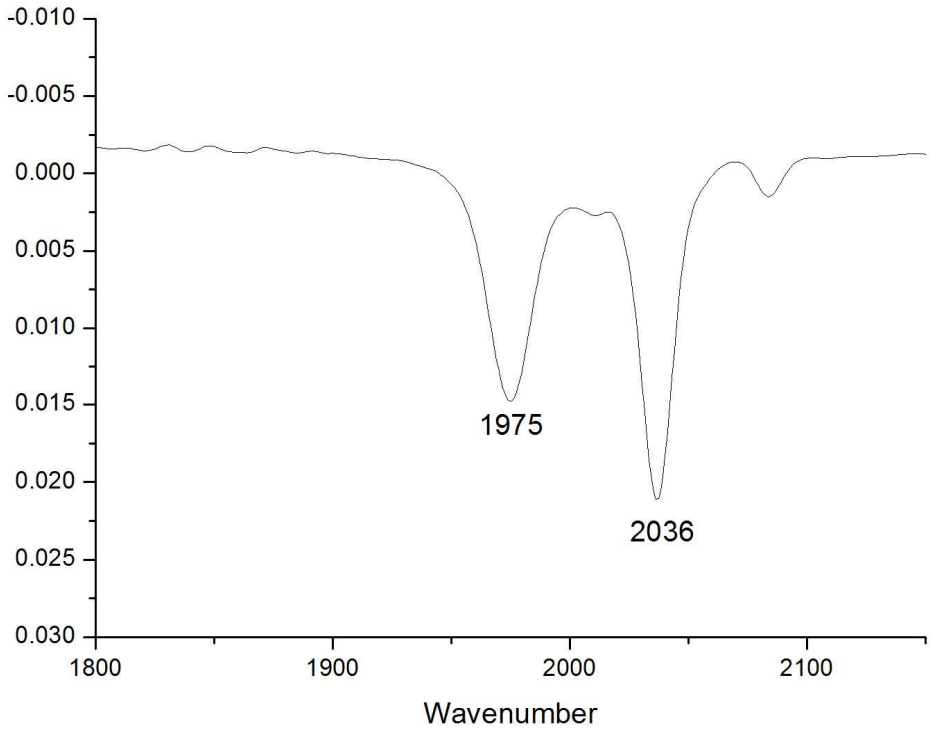

Figure S7. IR spectrum of **3b'** in $CHCl_3$.

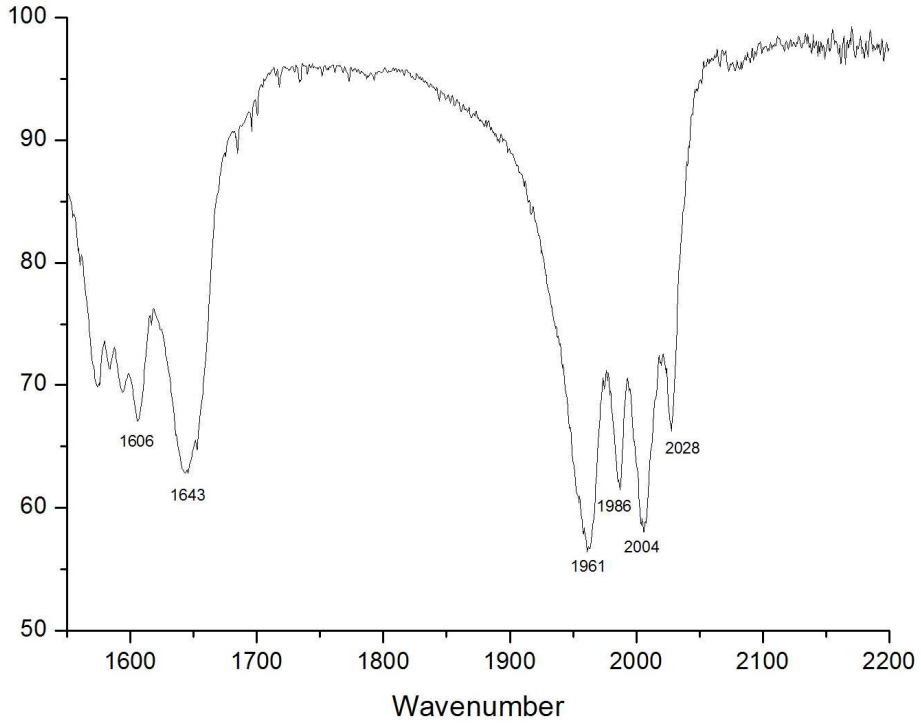

Figure S8. IR spectrum of **3c** in the solid state.

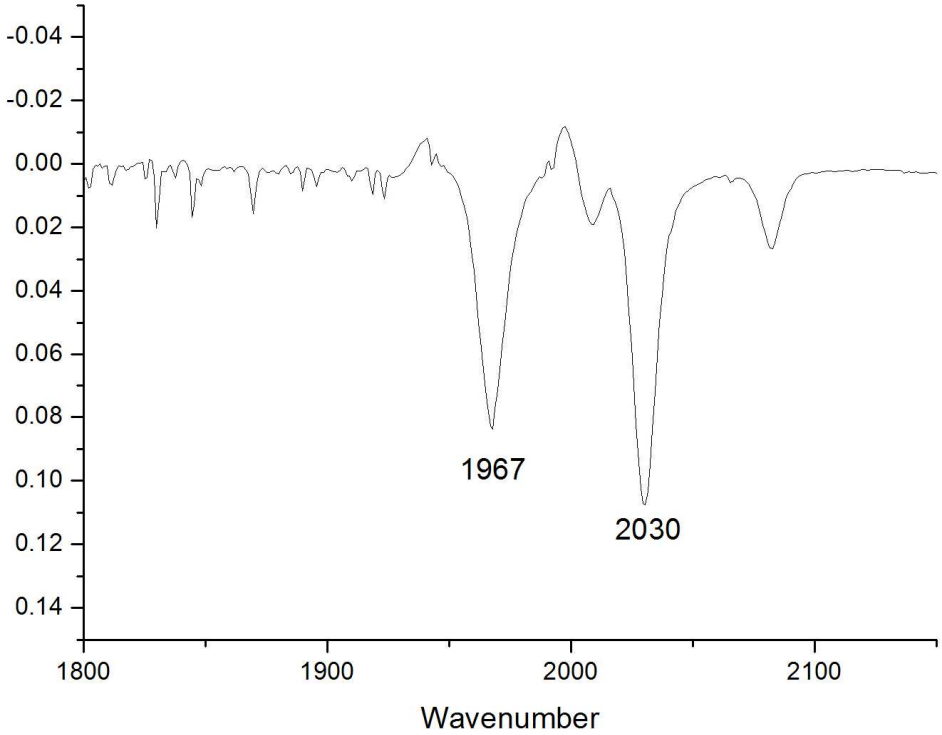

Figure S9. IR spectrum of **3c'** in CH_3CN.

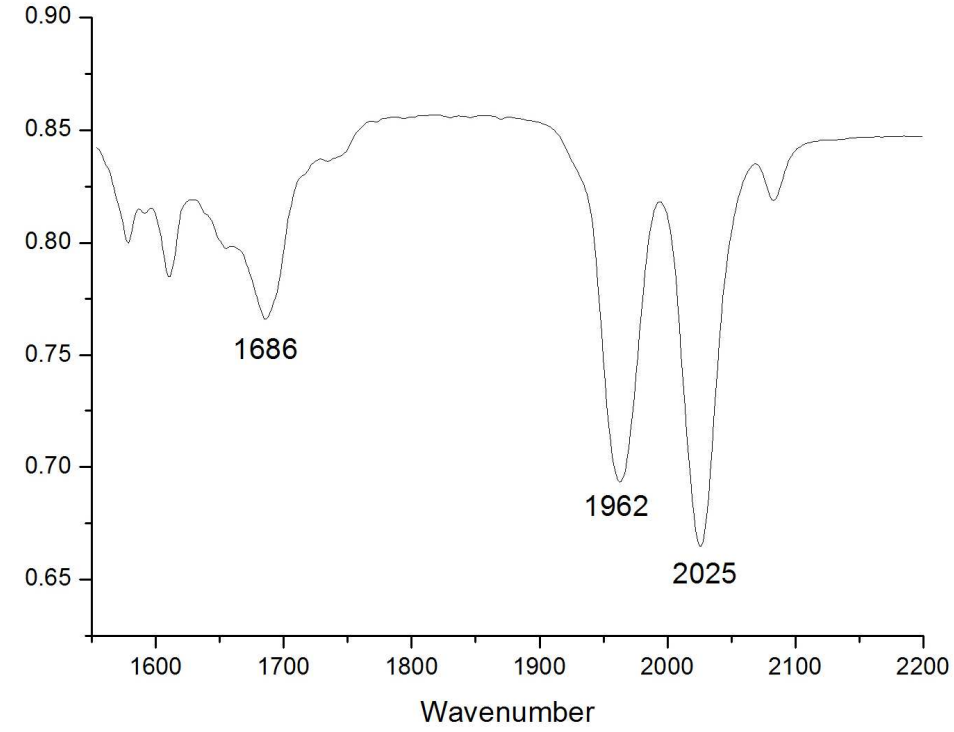

Figure S10. IR spectrum of **3d'** in the solid state.

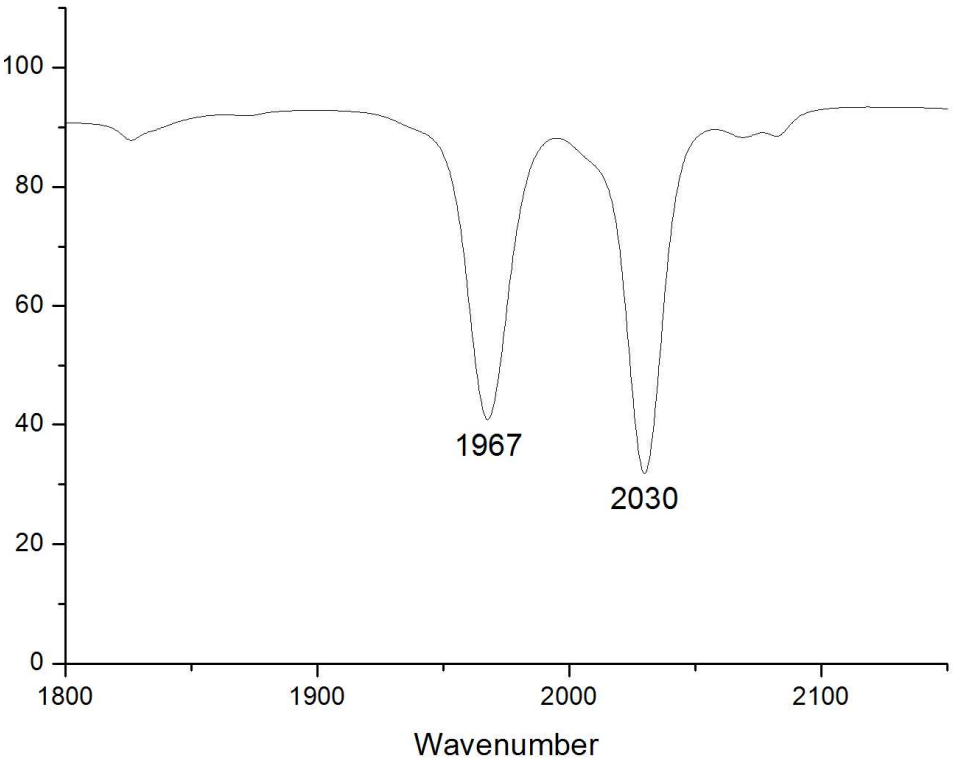

Figure S11. IR spectrum of **3d'** in CH_3CN.

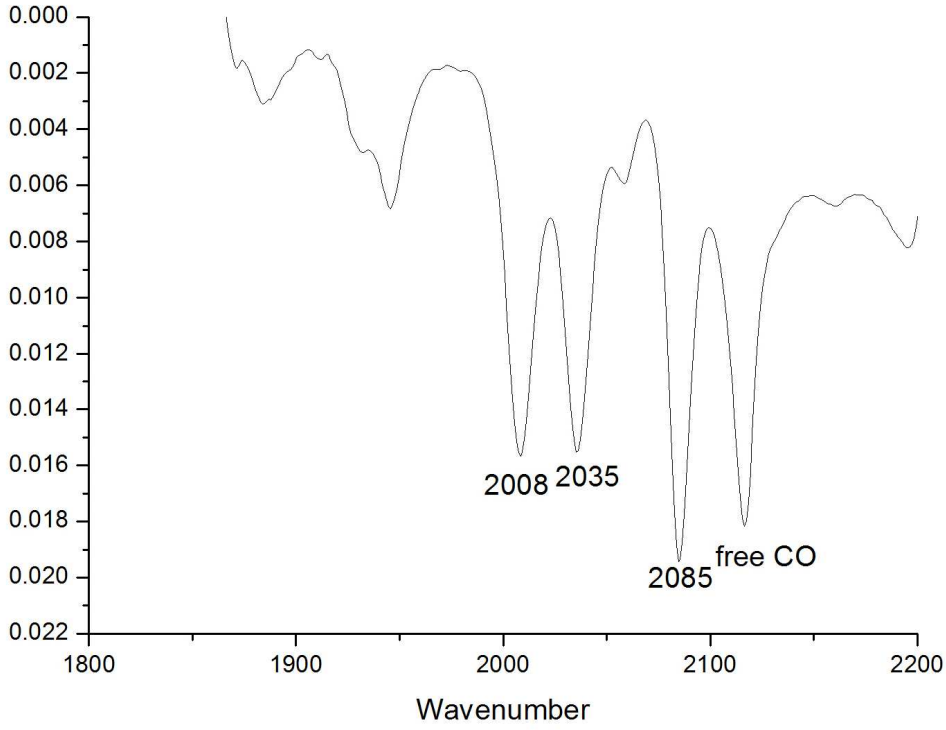

Figure S12. IR spectrum of **5d** in CH_3CN.

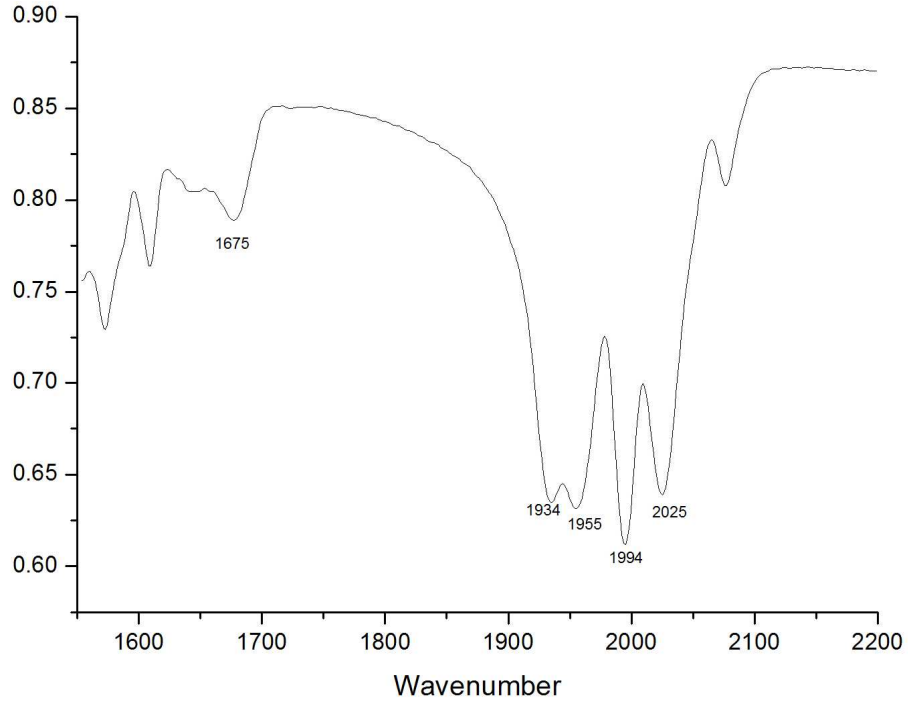

Figure S13. IR spectrum of **3e** in the solid state.

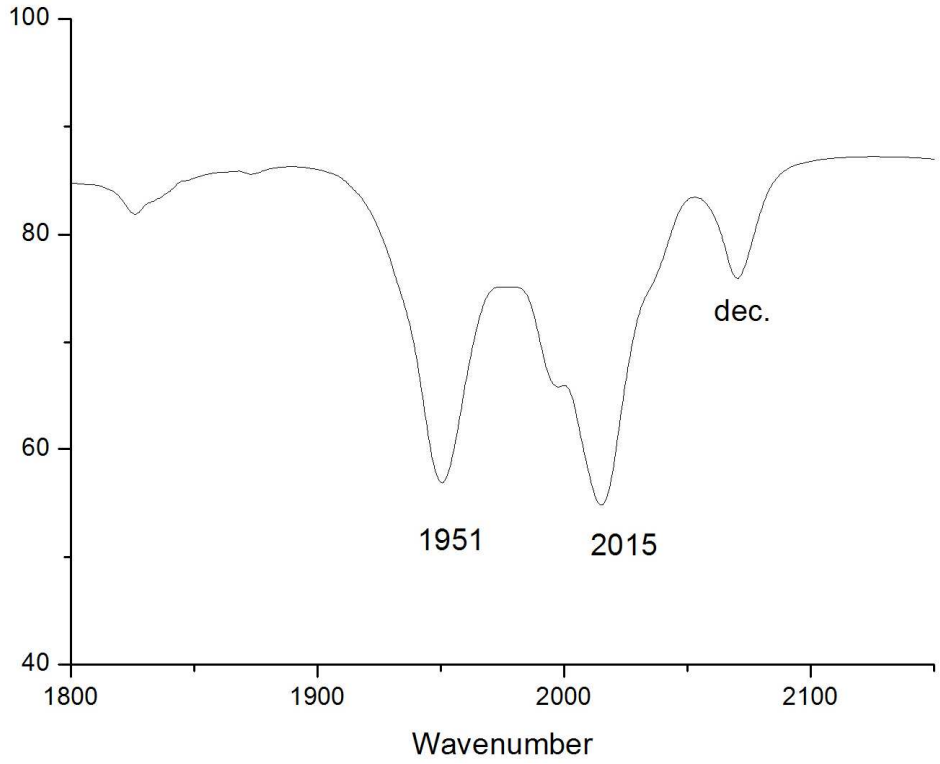

Figure S14. IR spectrum of **3e'** in CH_3CN.

NMR spectra

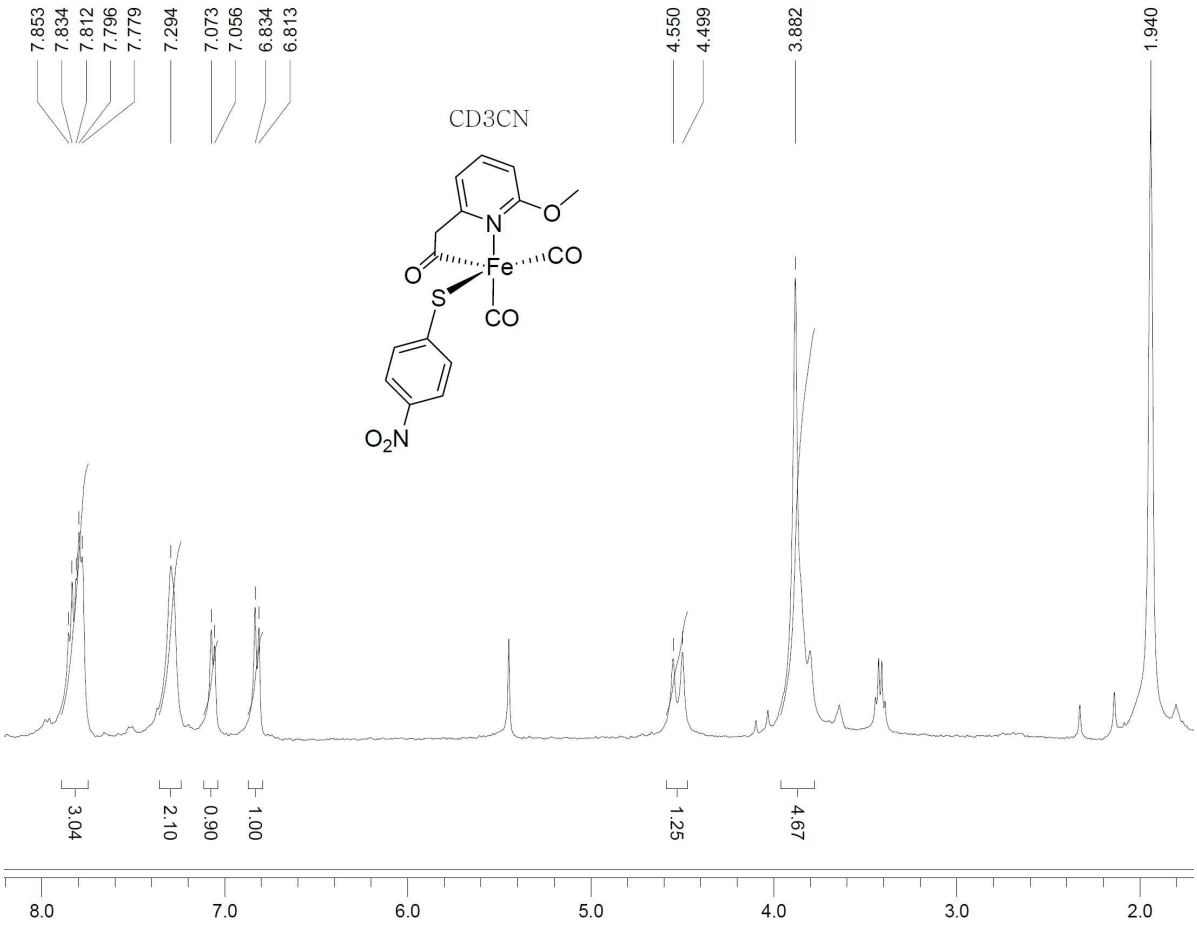

Figure S15. ^{1}H NMR spectrum of **3a'** in CD_3CN at room temperature.

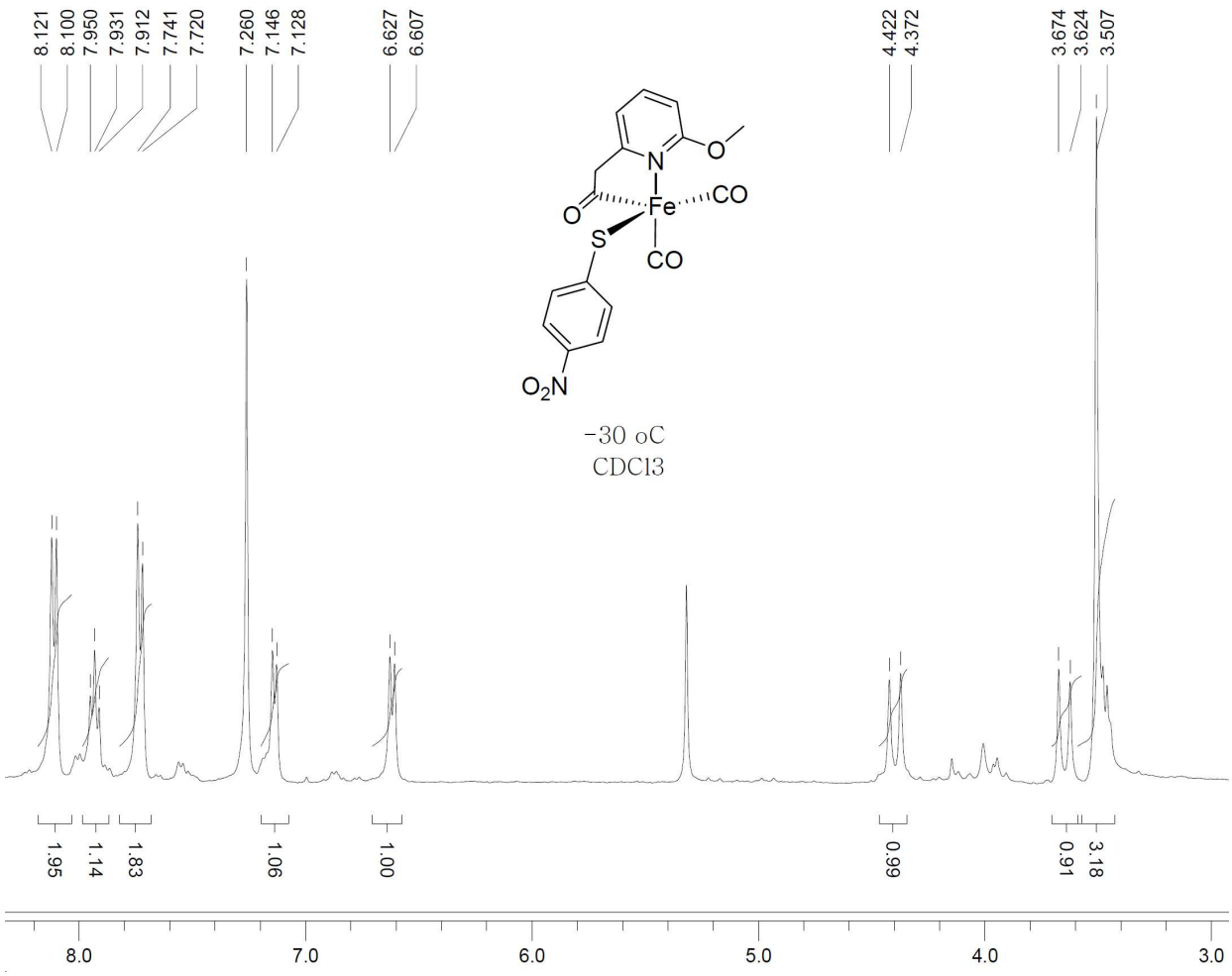

Figure S16. ^{1}H NMR spectrum of **3a'** in $CDCl_3$ at -30 ^{o}C.

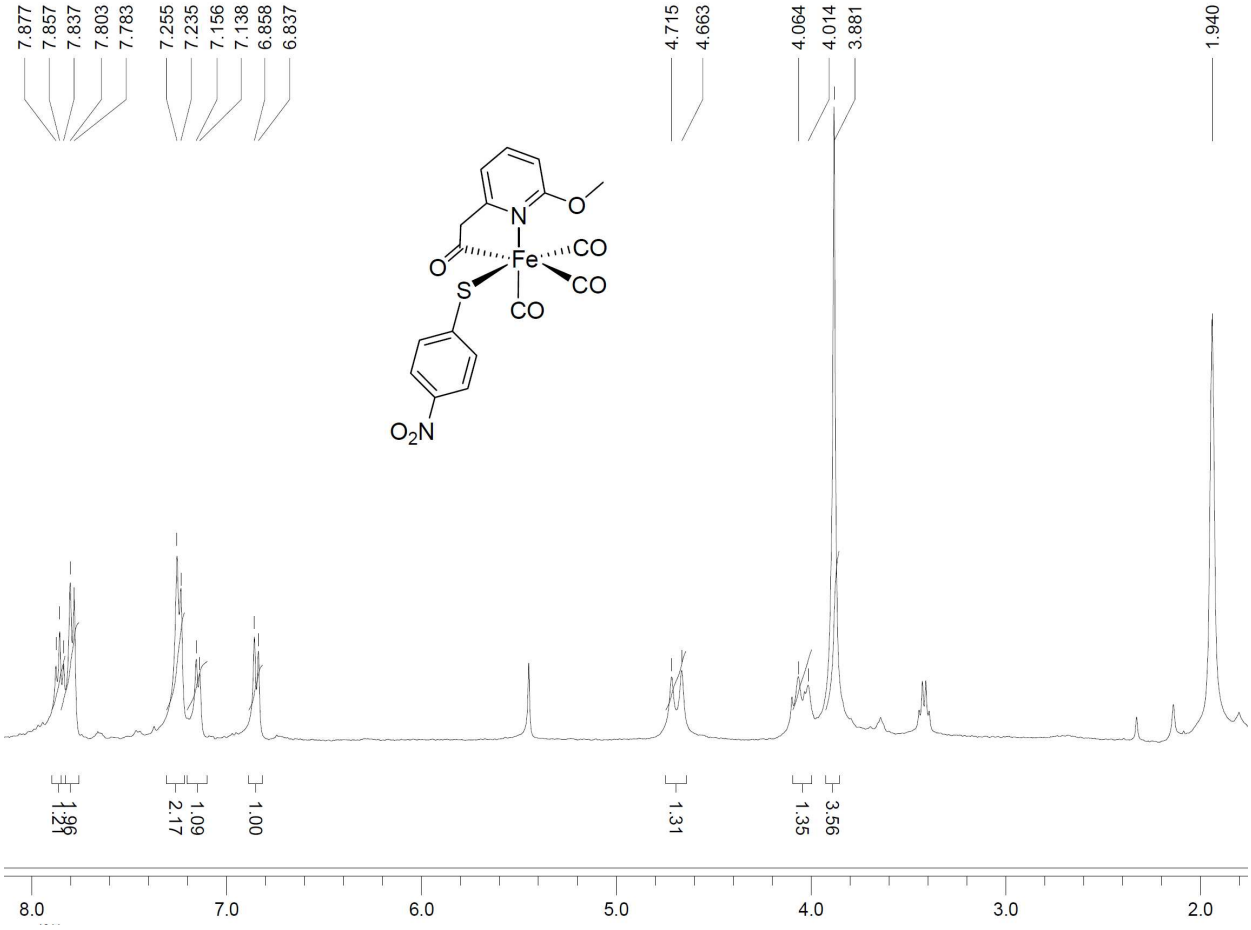

Figure S17. ^{1}H NMR spectrum of **5a** in CD_3CN at room temperature.

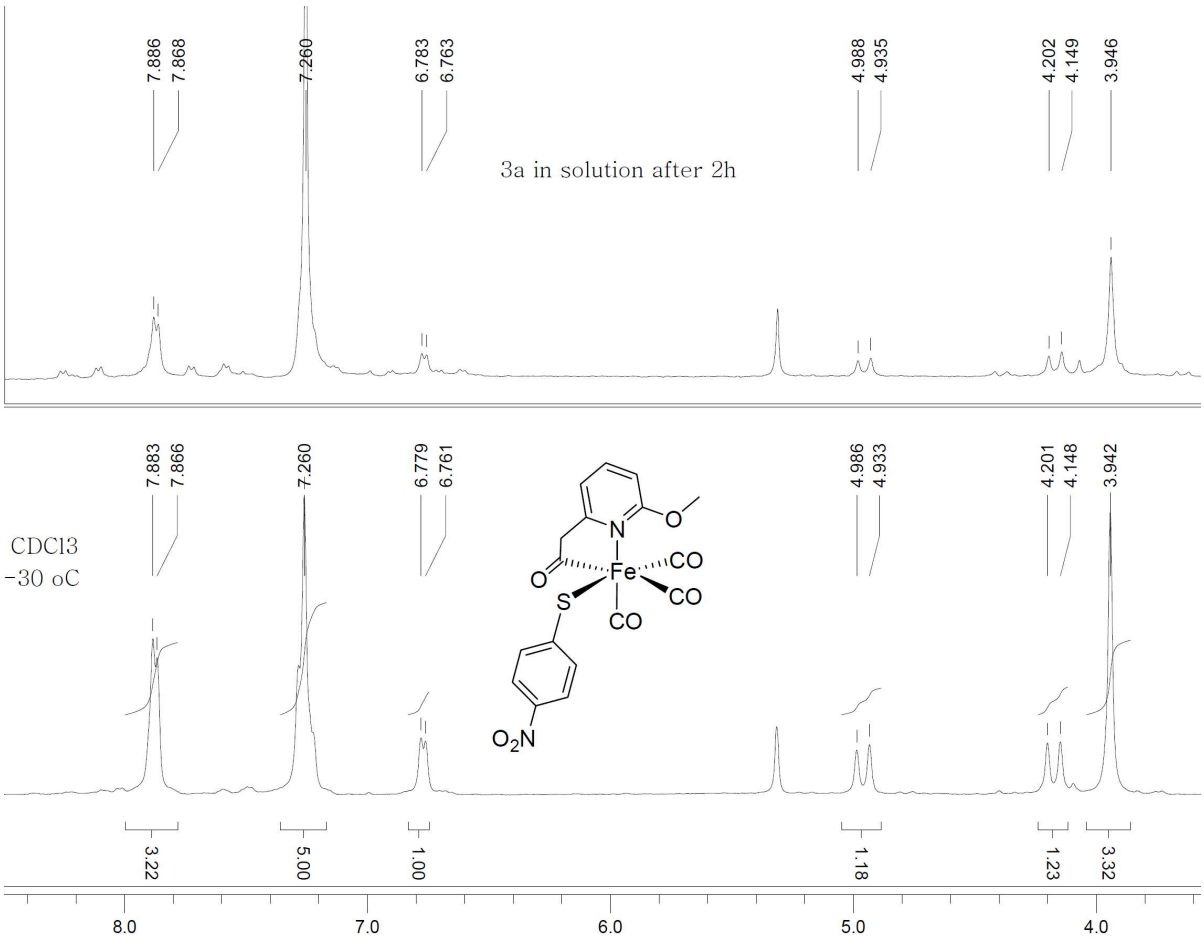

Figure S18. Top: After left in $CDCl_3$ for 2h, the ^1H NMR spectrum of **3a'** at -30 ^oC; bottom: ^1H NMR spectrum of **5a** in $CDCl_3$ at -30 ^oC.

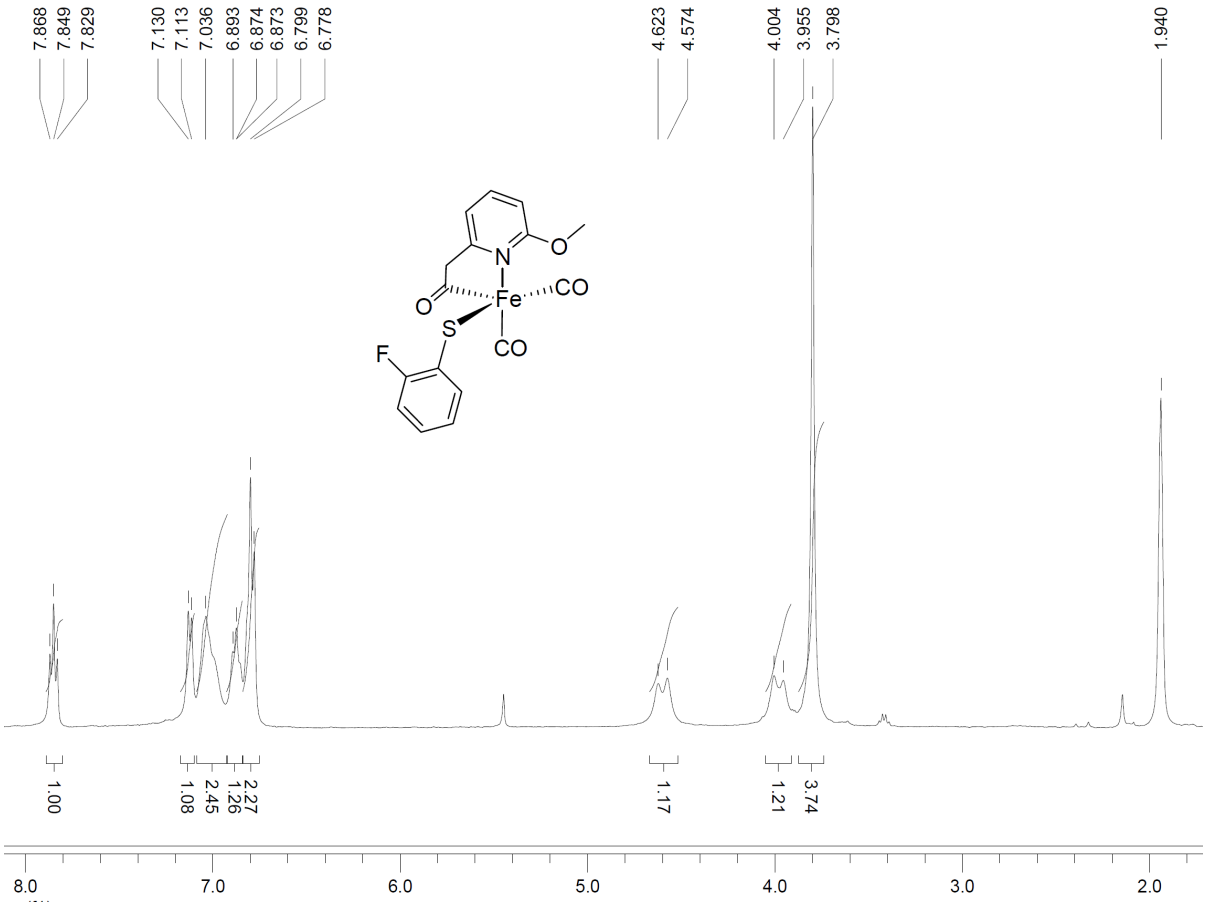

Figure S19. ^{1}H NMR spectrum of **3b'** in CD_3CN at room temperature.

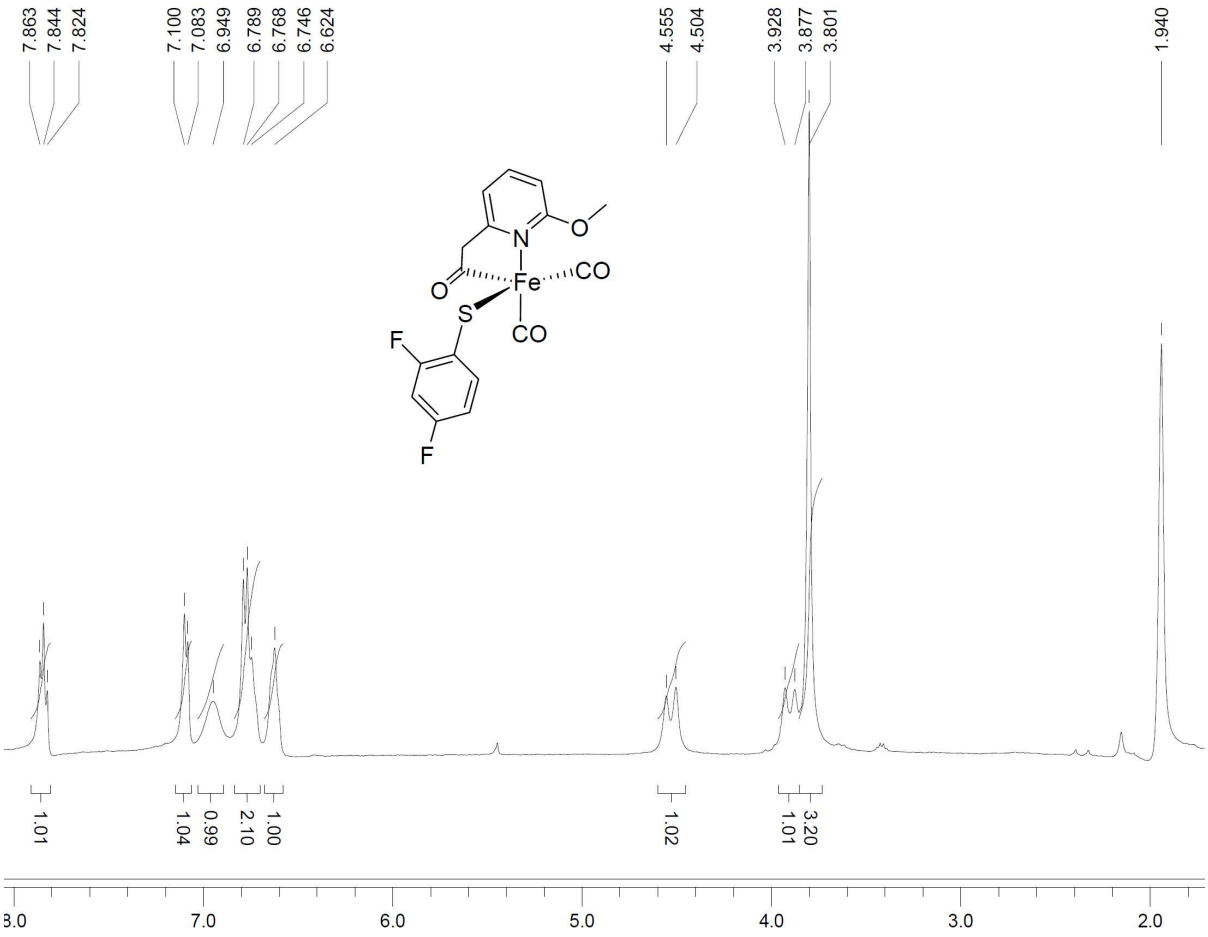

Figure S20. ^{1}H NMR spectrum of **3c'** in CD_3CN at room temperature.

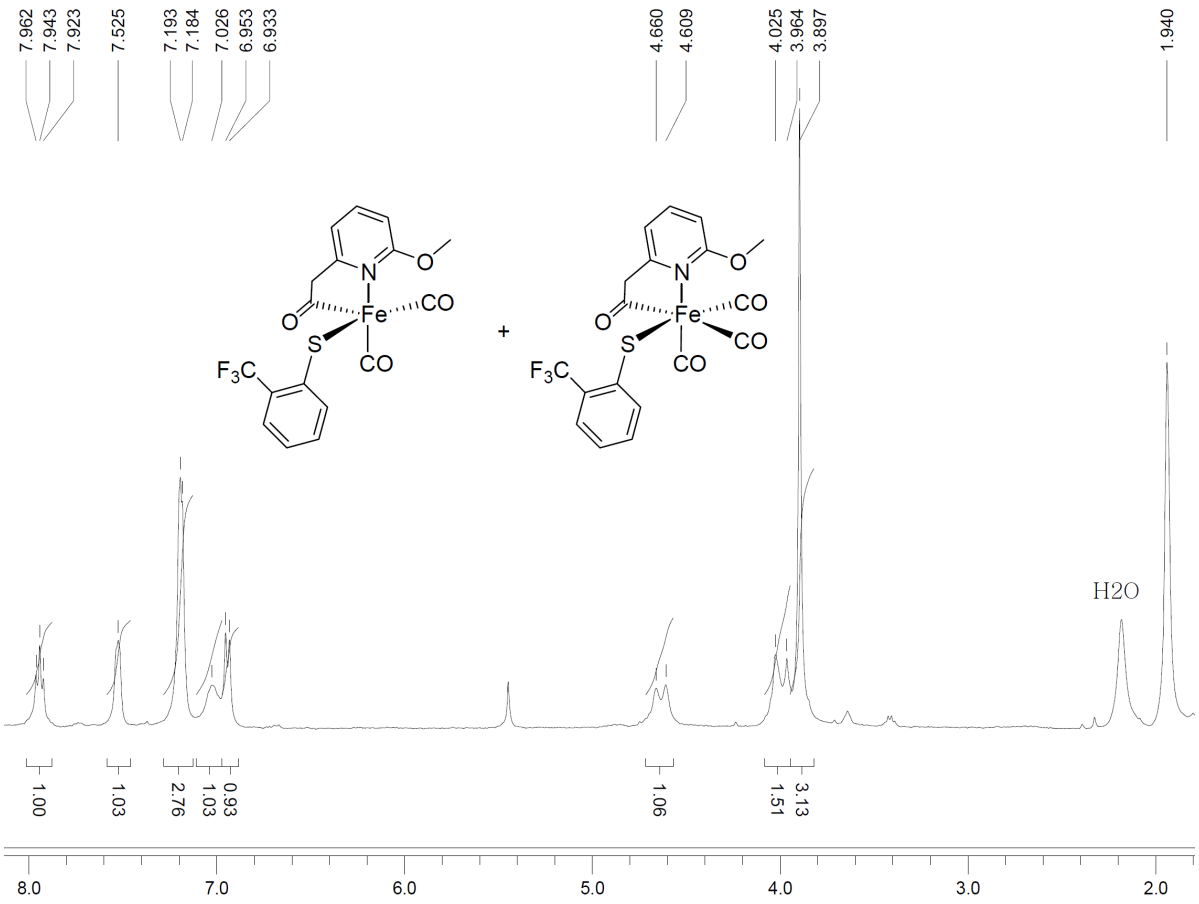

Figure S21. ^{1}H NMR spectrum of the mixture of **3d'** and **5d** in CD_3CN at room temperature.

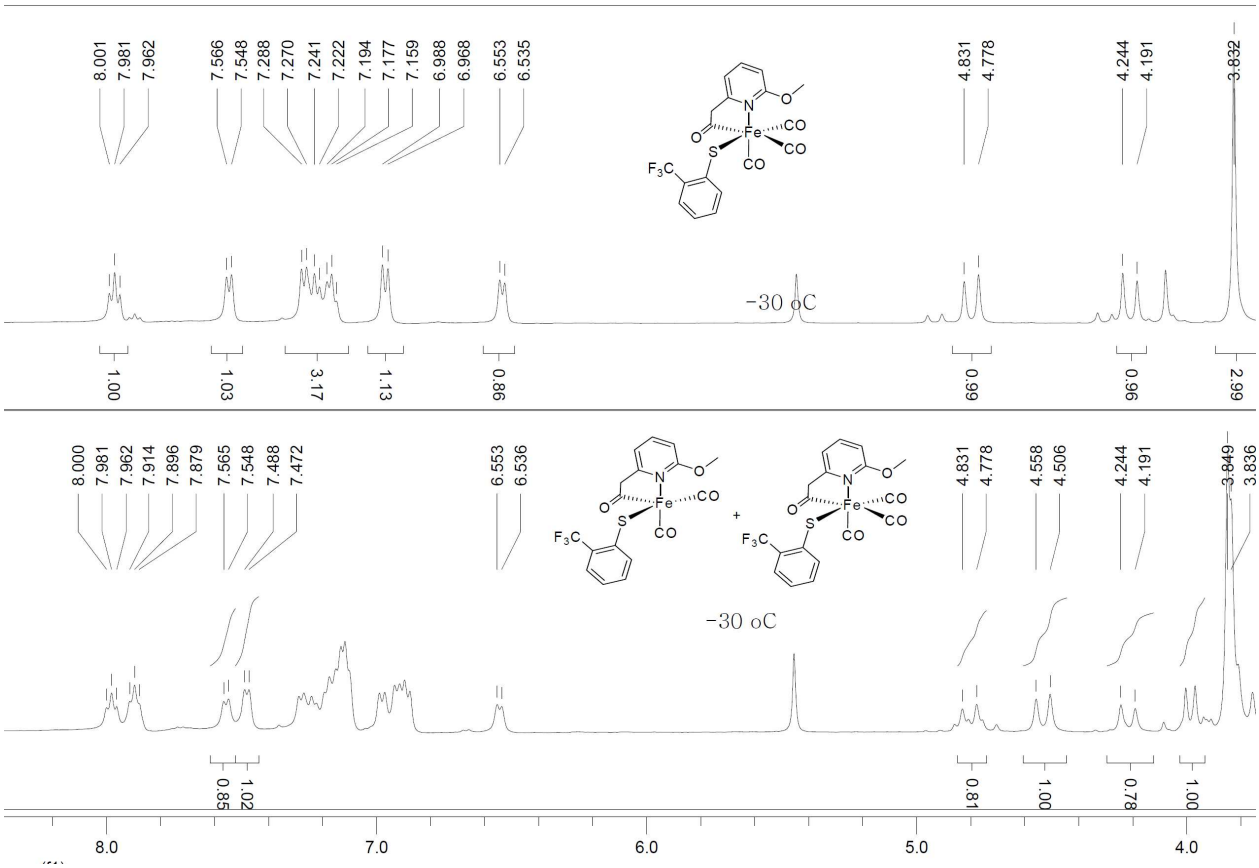

Figure S22. Top: ^{1}H NMR spectrum of **5d** in CD_3CN at -30 ^{o}C;
bottom: ^{1}H NMR spectrum of **3d' + 5d** in CD_3CN at -30 ^{o}C.

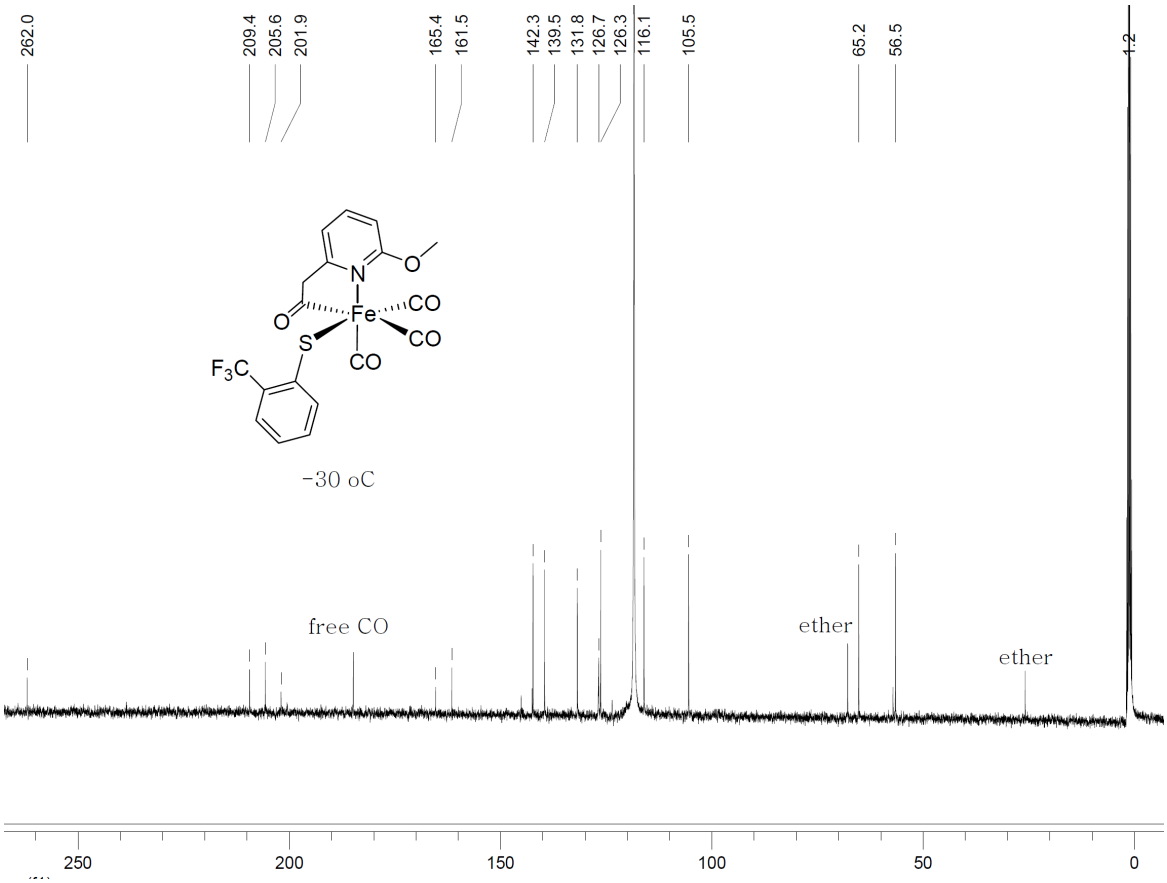

Figure S23. ^{1}H NMR spectrum of **5d** in CD_3CN at -30 ^{o}C.

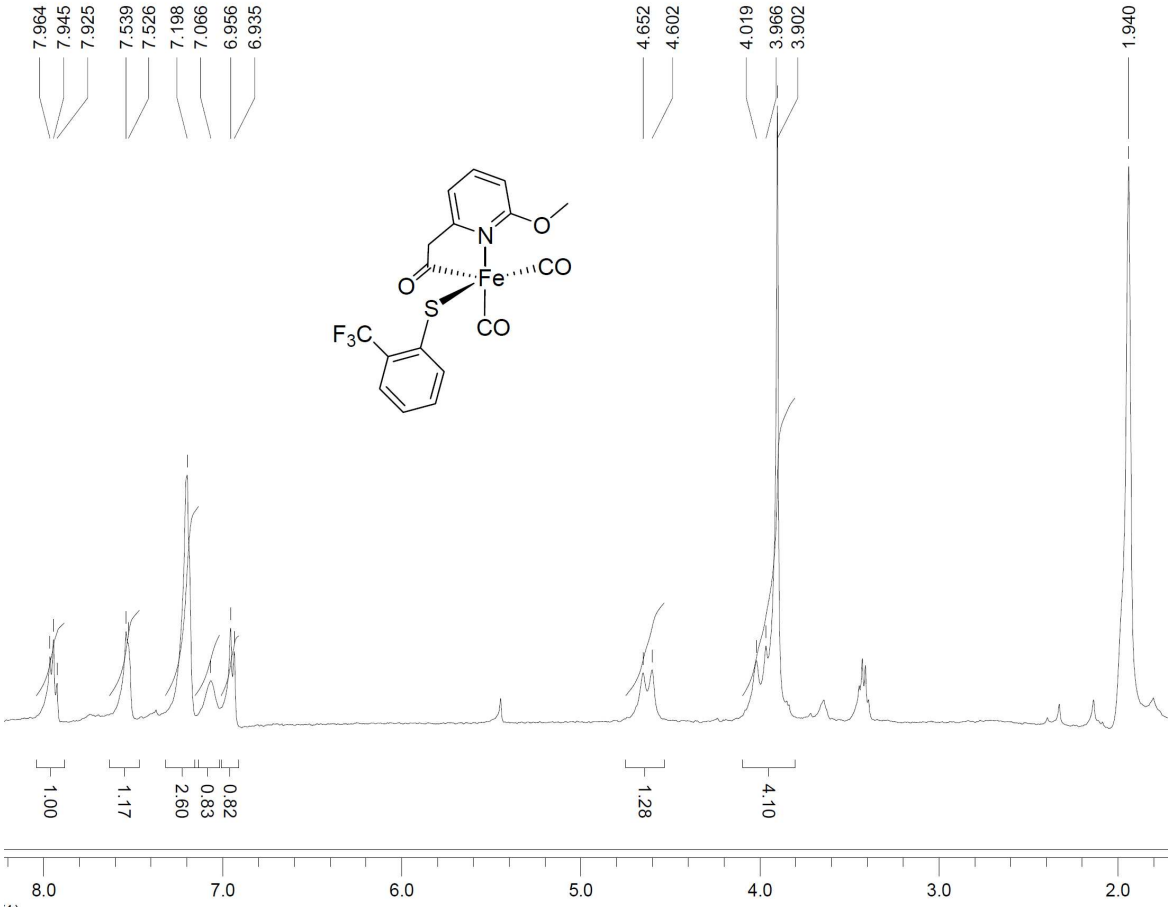

Figure S24. ^{1}H NMR spectrum of **3d'** in CD_3CN at room temperature.

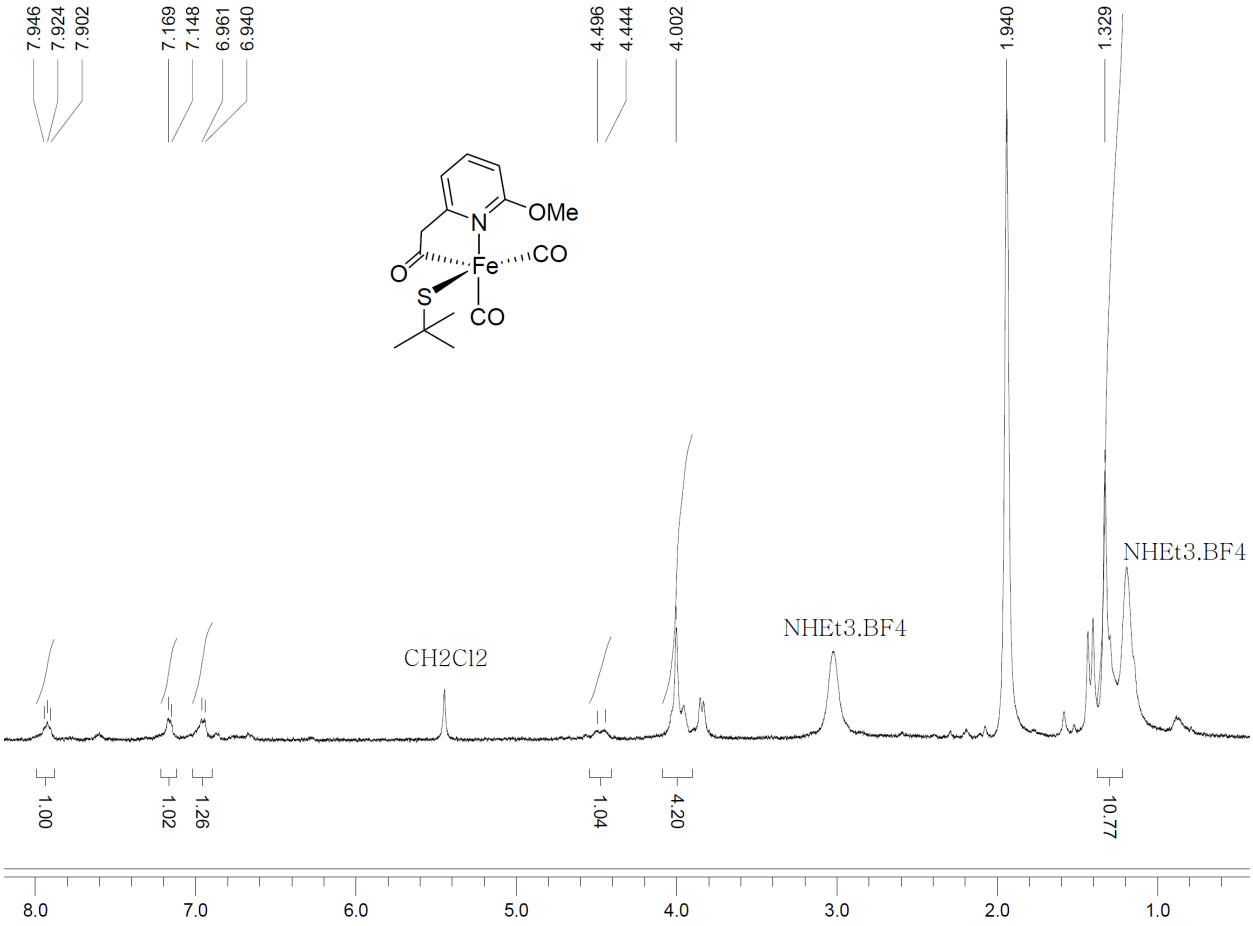

Figure S25. ^{1}H NMR spectrum of **3e'** and $[NEt_3H]BF_4$ in CD_3CN at room temperature.